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<p>(21) International Application Number: <b>PCT/US99/23879</b> (22) International Filing Date: <b>14 October 1999 (14.10.99)</b> (30) Priority Data: 60/104,452      16 October 1998 (16.10.98)      US 60/104,985      20 October 1998 (20.10.98)      US (71) Applicant: <b>EXXON CHEMICAL PATENTS INC. (US/US);</b> 5200 Bayway Drive, Baytown, TX 77520-5200 (US). (72) Inventor: <b>MACKAY, John, H.;</b> 910 Bristol Trail Road, Lake Zurick, IL 60047 (US). (74) Agent: <b>ELLIOTT, Douglas, H.; Tobor, Goldstein &amp; Healey,</b> L.L.P., Suite 2300, 1360 Post Oak Boulevard, Houston, TX 77056 (US).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report.</i></p>
<p>(54) Title: <b>PROCESS FOR PRODUCING POLYOLEFIN MICROPOROUS BREATHABLE FILM</b></p> <div data-bbox="373 1134 1185 1701"></div> <p>(57) Abstract</p> <p>Polyolefin/filler breathable films may be produced by machine or transverse direction orientation using interdigitating grooved rollers (16, 26). Biaxial orientation to similarly produce breathable films may be accomplished by the same method. By heating the rollers (16, 26), the breathability of the film is increased without increasing the depth of engagement of the interdigitating rollers.</p>		

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## PROCESS FOR PRODUCING POLYOLEFIN MICROPOROUS BREATHABLE FILM

### RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application serial number 60/104,452 filed October 16, 1998 and U.S. Provisional Patent Application serial number 60/104,985 filed October 20, 1998.

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### BACKGROUND OF THE INVENTION

#### Field

This invention relates generally to an improved polyolefin microporous breathable film and method of making same. More specifically, this invention is directed toward a process by which increased Water Vapor Transmission Rate (WVTR) and enhanced film appearance can be realized with substantially the same film formulation and orientation.

10

#### Background

Preparation of films having good WVTR from highly filled polymers, usually polyolefins, is well known in the art. In the past, a combination of polyolefin, usually a polyethylene, with a filler, usually  $\text{CaCO}_3$ , is widely used as a film with good WVTR, often, but not necessarily, in combination with non-woven polymers for use in diapers, adult incontinence devices, feminine hygiene articles, surgical garments, housewrap composites, protective apparel, roofing materials and the like.

15

The use of interdigitating rolls to orient films or non-wovens is also well known in the art. In some cases this process is referred to as cold stretching. To increase the WVTR of films, while employing interdigitating technology, it has been necessary to increase the level of filler in the polyolefin/filler blend, or to increase the depth of interengagement of the orienting rollers

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– both of which have technical limits, and which may have a serious negative impact on important physical properties of the resulting film. The technical limits of depth of engagement of the interdigitating rolls and  $\text{CaCO}_3$  loading restrict film breathability level.

Also, it is desirable for many applications of breathable film, such as disposable diapers, adult incontinence products, and feminine hygiene devices, that some visual evidence of a difference between breathable and non-breathable films exist. It is thought that this product differentiation could be of benefit to the consumer, as well as the manufacturer of the disposable products.

### **SUMMARY**

We have discovered that applying heat to interdigitating rollers results in a substantial improvement in orientation effectiveness (WVTR increases), and imparts a third dimensionality to the film which differentiates it from other breathable films. In addition, a new control is provided for the adjustment of film breathability, i.e., rather than require a formulation change, or adjustment to the depth of activation of the interdigitating rollers, to control WVTR levels, roller temperature may be adjusted. As can be seen from the following examples, with all other factors constant, an increase in the temperature of the interdigitating rolls from 70°F to 140°F, increases WVTR from 1900 gm/sqm/day to 4100 gm/sqm/day.

### **Brief Description of the Drawings**

A better understanding of the Process for Producing Polyolefin Microporous Breathable Film may be obtained by reference to the following drawing figures together with the detailed description.

Figure 1 shows the geometry of interdigitating rollers;

Figure 2 shows a machine direction orientation roller;

Figure 3 shows a transverse direction orientation roller; and

Figure 4 shows a cross-section of a WVTR test cell.

## **DETAILED DESCRIPTION**

### **Introduction**

5           This invention concerns polyolefin/filler based breathable films. While initial work was executed on a polypropylene based product, it will be shown that the disclosed process is effective for all polyolefin materials.

          This invention further includes certain polyolefins, their conversion into fabricated articles such as films, articles made from such films, and applications in which such articles  
10   having high WVTR combined with good physical properties are desirable. The resulting films, and film composites, (including coextruded and laminated films) have combinations of properties rendering them superior and unique to films or film composites previously available. The films disclosed herein are particularly well suited for use in producing certain classes of high WVTR films, consumer and industrial articles using the films in combination with, for instance,  
15   polymeric woven or non-woven materials. Such consumer articles include, but are not limited to diapers, adult incontinence devices, feminine hygiene articles, medial and surgical gowns, medical drapes, industrial apparel, building products such as "house-wrap", roofing components, and the like made using one or more of the films disclosed herein. Additionally, the films of the present invention may also be used in metallized films with a high WVTR, according to the  
20   disclosure of U.S. Patent 5,055,338, which is to be incorporated herein by reference in its entirety.

**Production of the Films**

Films contemplated by certain embodiments of the present invention may be made utilizing a polyolefin, by film processes including blown molding, casting, and cast melt embossing. The preferred process is a cast melt embossed film process. In extrusion processes, the films of the present invention can be formed into a single layer film, or may be one layer or more of a multi-layer film or film composite. Alternatively, the polyolefin films described in this disclosure can be formed or utilized in the form of a resin blend where the blend components can function to modify the WVTR, the physical properties, the draw-down, the sealing, the cost, or other parameters. Both blend components and the parameters provided thereby will be well known to those of ordinary skill in the art. The breathable films of the present invention may also be included in laminated structures. As long as a film, multi-layer film, or laminated structure includes one or more polyolefin/filler film layers having the WVTR, or draw-down, and the like of the film, such film, multi-layer film, or laminated structure will be understood to be contemplated as an embodiment of the present invention.

**Polyolefin Precursor Film Component**

The polyolefin precursor component can be any film forming polyolefin including polyethylene and polypropylene, ethylene polar comonomer polymers, ethylene  $\alpha$ -olefin copolymers and combinations hereof.

Suitable Polyolefins and Relative Benefits				
Polypropylene	Impact	Tear	Softness	Drawdown
Metallocene Homopolymers and Copolymers	preferred	preferred	preferred	most preferred
Random Copolymer PP	more preferred	more preferred	more preferred	more preferred
Impact Copolymer polypropylene	most preferred	most preferred	most preferred	preferred
Homopolymer PP	preferred	preferred	preferred	preferred
Exxon LD 3003	preferred	preferred	preferred	preferred

10 It will be understood that, in general, we contemplate that a large number of polyolefins  
 will be useful in the techniques and applications described herein. Also included in the group  
 of polyolefins that are contemplated as embodiments of this invention are metallocene catalyzed  
 polyethylenes, both linear low density and very low density (0.88 to 0.935 g/cm<sup>3</sup>), high density  
 polyethylene (0.935 – 0.970 g/cm<sup>3</sup>), Ziegler-Natta catalyzed linear low density polyethylene,  
 15 conventional high pressure low density polyethylene (LDPE), and combinations thereof. Various  
 elastomers or other soft polymers may be blended with the majority polyolefin component, these  
 include styrene-isoprene-styrene (styrenic block co-polymer), styrene-butadiene-styrene (styrenic  
 block co-polymer), styrene-ethylene/butylene-styrene (styrenic block co-polymer), ethylene-  
 propylene (rubber), Ethylene-propylene-diene-modified (rubber), Ethylene-vinyl-acetate,  
 20 Ethylene-methacrylate, Ethylene-ethyl-acrylate, Ethylene-butyl-acrylate.

### **FILLER**

Fillers useful in this invention may be any inorganic or organic material having a low  
 affinity for and a significantly lower elasticity than the film forming polyolefin component.  
 Preferably a filler should be a rigid material having a non-smooth hydrophobic surface, or a  
 25 material which is treated to render its surface hydrophobic. The preferred mean average particle

size of the filler is between about 0.5-5.0 microns for films generally having a thickness of between about 1 to about 6 mils prior to stretching.

Examples of the inorganic fillers include calcium carbonate, talc, clay, kaolin, silica, diatomaceous earth, magnesium carbonate, barium carbonate, magnesium sulfate, barium sulfate, calcium sulfate, aluminum hydroxide, zinc oxide, magnesium hydroxide, calcium oxide, magnesium oxide, titanium oxide, alumina, mica, glass powder, zeolite, silica clay, etc. Calcium carbonate ( $\text{CaCO}_3$ ) is particularly preferred for its low cost, its whiteness, its inertness, and its availability. The selected inorganic filler such as calcium carbonate is preferably surface treated to be hydrophobic so that the filler can repel water to reduce agglomeration. Also, the surface treatment of the filler should improve binding of the filler to the polyolefin precursor while allowing the filler to be pulled away from the precursor film under stress. A preferred coating for the filler is calcium stearate which is FDA compliant and readily available.

Organic fillers such as wood powder, and other cellulose type powders may be used. Polymer powders such as Teflon® powder and Kevlar® powder can also be used.

The amount of filler added to the polyolefin precursor depends on the desired properties of the film including dart impact strength, tear strength, WVTR, and stretchability. However, it is believed that a film with good WVTR generally cannot be produced as is taught herein with an amount of filler less than about twenty percent (20%) by weight of the polyolefin/filler blend.

The minimum amount of filler (about twenty percent by weight) is needed to assure the interconnection within the polyolefin precursor film of voids created at the situs of the filler – particularly by the stretching operation to be subsequently performed. Further, it is believed that useful films could not be made with an amount of the filler in excess of about seventy percent (70%) by weight of the polyolefin/filler composition. Higher amounts of filler may cause



difficulty in compounding and significant losses in strength of the final breathable film. Preferred ranges include about 30% to about 70% by weight, more preferably from about 40% to about 60% by weight.

While a broad range of fillers has been described at a broad range of inclusion parameters based on weight percentages, still other embodiments of the present invention are contemplated. For instance, fillers with much higher or much lower specific gravity may be included with the polyolefin precursor at amounts outside the weight ranges disclosed. Such combinations will be understood to be contemplated as embodiments of our invention as long as the final film, after orientation, has WVTR, or draw down similar to that described herein.

#### Film Physical Property Modification

It was found that the addition of small amounts of low density polyethylene to the polyolefin/filler blend allowed film extrusion at higher throughput levels with some majority polymers. Low density polyethylene with a melt flow index of about 0.9 to 25.0 grams per ten minutes (12.0 grams per ten minutes being preferred), and a density of about 0.900 to 0.930 may be used.

Further improvements in film impact and tear strength are possible by the addition of plastomers, elastomers, styrenic block co-polymers (SIS, SBS, SEBS), or rubbers. Material grades included are:

Property Improvement Materials			
Supplier	Grade	Melt Flow Index	Density
Exxon Chemical	Exact 3139	7.5	.900
Exxon Chemical	Exact 4044	16.5	.895
Exxon Chemical	Exact 9095	2.2	.893
Exxon Chemical	Exact 3131	3.5	.900
Exxon Chemical	Paxon SLX 9106	2.0	.900

Exxon Chemical	Paxon SLX 9101	3.5	.900
Dexco	Vector 4211	13	
Dexco	Vector 4411	40	
Exxon	Vistalon 3708		
Exxon	Vistalon 3030		
Shell	Kraton G1657	8	SEBS
Union Carbide	UC 9042	5.1	.900
Union Carbide	UC 1085	0.8	.884

### 10 Stretching or Orienting

Final preparation of a breathable film is achieved by stretching the filled polyolefin precursor film to form interconnected voids. Stretching or "orientation" is achieved by incrementally orienting the polyolefin precursor in the machine direction, transverse direction, or both. Films can be incrementally oriented by a number of mechanical techniques, however, the preferred technique is to stretch the film through pairs of interdigitating rollers, as shown in Figure 1. Therein it may be seen that the film is contracted by the apex 18 of a plurality of teeth spaced a distance or pitch (W) apart. The apex 18 of each tooth extends into the open space 20 between the teeth on an opposing roller. The amount of interengagement depends both on the tooth depth (d) and the relative position of the rollers.

Machine direction orientation is accomplished by stretching the film through a gear like pair of rollers 16 as shown in Figure 2. Transverse direction orientation is accomplished by stretching the film through a pair of disk-like rollers as shown in Figure 3.

The preferred embodiment employs rollers with a tooth pitch,  $W = 0.080''$ , however a pitch of about  $0.040''$  to  $0.500''$  is also acceptable. The tooth depth (d), is preferably  $0.100''$ , however, a tooth depth of about  $0.030''$  to  $0.500''$  is also acceptable. For the transverse direction orientation rollers, as shown in Figure 3, the depth may be up to about  $1.000''$  as mechanical

interference is less of an issue with the transverse direction rollers. The preferred embodiment employs interdigitating rollers that can be temperature controlled from about 50°F to about 210°F. More preferred is a temperature range of from about 70°F to about 190°F. Even more preferred is a temperature range from about 85°F to about 180°F. And most preferred is a temperature range from about 95°F to about 160°F. Roll temperature may be maintained through the internal flow of a heated or cooled liquid, an electrical system, an external source of cooling/heating, combinations thereof, and other temperature control and maintenance methods which will be apparent to those of ordinary skill in the art. The preferred embodiment is internal flow of a heated or cooled liquid through the rollers.

The depth of interengagement of the roller teeth determines the amount of orientation imparted on the film. A balance must be drawn between the depth of engagement of the roller teeth and the level of filler in the film, as many physical properties of the film are affected as depicted in the following table.

**Relationships between process and formulation factors**

	Adjust	WVTR	Dart Impact	Basis Weight	CD Tensile	MD Tear
CaCO <sub>3</sub>	Increase	Increase	Increase			decrease
MD Orientation	Increase	Increase	decrease	decrease		decrease
TD Orientation	Increase	Increase	decrease	decrease	Decrease	
Roll Temperature	Increase	Increased		decrease		

### **Properties of Films Produced**

#### **WVTR**

In an embodiment of the present invention, certain films and articles made therefrom have higher WVTR than previously thought possible. The WVTR of such films should be above

about 100 g/m<sup>2</sup>/24 hr @ 37.8°C, 100% RH, preferably above about 1000 g/m<sup>2</sup>/24 hr @ 37.8°C, 100% RH, more preferably above about 2000 g/m<sup>2</sup>/24 hr @ 37.8°C, 100% RH. Some applications benefit from film with a WVTR at or above about 10,000 g/m<sup>2</sup>/24 hr @ 37.8°C, 100% RH.

## 5 **TEST METHODS**

### Water Vapor Transmission Rate (WVTR)

Both a Mocon W1, and a Mocon W600 instrument are used to measure water evaporated from a sealed wet cell at 37.8°C through the test film and into a stream of dry air or nitrogen. It is assumed that the relative humidity on the wet side of the film is near 100%, and the dry side  
10 is near 0%. The amount of water vapor in the air stream is precisely measured by a pulse modulated infra red (PMIR) cell. Following appropriate purging of residual air, and after reaching a steady state of water vapor transmission rate, a reading is taken. WVTR of the test films are reported at Grams of Water/Meter<sup>2</sup>/Day @ 37°C. The output of the unit has been calibrated to the results obtained with a film of known WVTR. The testing protocols are based  
15 on ASTM 1249-90 and the use of a reference film, such as Celgard 2400, which has a WVTR of 8700 g/m<sup>2</sup>/day @ 37.8°C. The diagram depicted in Figure 4 illustrates the basic operation of the Mocon units.

### Mocon W1

As illustrated generally by reference to Figure 4, the Mocon W1 has a single test cell and  
20 an analog chart recorder. Air is pumped through a desiccant dryer, then through the test cell, and then past the PMIR sensor. A five-minute purge of residual air is followed by a six-minute test cycle with controlled air flow. The result is a steady state value for WVTR. The purge and test cycles are controlled manually. The unit is calibrated to a film with a known WVTR every

twelve hours. Calibration results are control charted and adjustments are made to the instrument calibration accordingly.

#### Mocon W600

The Mocon W600 has six measurement cells with PMIR data fed into a computer. Nitrogen is fed through a desiccant dryer, then through the active test cell, then past the PMIR sensor. In addition to data compilation, a computer controls test cycle sequencing. All cells are purged simultaneously for an eight-minute period. This is followed by an eight-minute test cycle for each of the six measurement cells. Total testing time is fifty-six minutes. Two of the six measurement cells always measure reference films with a known WVTR.

#### 10 EXAMPLES

##### Example 1. Experimental grade 400-6-1

A blend of 57% ECC FilmLink 400  $\text{CaCO}_3$  was combined with 33% Exxon PD 7623 Impact Copolymer, 2% Exxon LD-200.48, and 8% Exxon Exact 3131 oriented in interdigitating rolls of 0.80" pitch. The MD depth of engagement was 0.020", and the TD depth of engagement was 0.040". The temperature of the interdigitating rolls was 140 °F.

##### Example 2. Experimental grade 400-6-2

A blend of 57% ECC FilmLink 400  $\text{CaCO}_3$  was combined with 33% Exxon PD 7623 Impact Copolymer, 2% Exxon LD-200.48, and 8% Exxon Exact 3131 oriented in interdigitating rolls of 0.080" pitch. The MD length of engagement was 0.020", and the TD depth of engagement was 0.040". The temperature of the interdigitating rolls was 110 °F.

##### Example 3. Experimental grade 400-6-3

A blend of 57% ECC FilmLink 400  $\text{CaCO}_3$  was combined with 33% Exxon PD 7623 Impact Copolymer, 2% Exxon LD-200.48, and 8% Exxon Exact 3131 oriented in interdigitating

rolls of 0.080" pitch. The MD depth of engagement was 0.020", and the TD depth of engagement was 0.040". The temperature of the interdigitating rolls was 70 °F.

As can be seen from the following table, the WVTR rise from a roll temperature of 70°F (considered ambient temperature) to 110°F, and then 140°F is dramatic, unexpected and surprising.

**Table of Example Film Properties**

	Example 1	Example 2	Example 3
Grade Number	400-6-1	400-6-2	400-6-3
Roll Temperature (°F)	140	110	70
Basis Weight (gm/sqm)	43	40	39
WVTR (gm/sqm/day)	4100	3000	1900
Dart Impact Strength (gm)	240	300	300
MD Ultimate (gm/in)	1585	1532	1453
MD Elongation (%)	408	431	442
TD @ 5% (gm/in)	457	389	388
TD Ultimate (gm/in)	785	1166	1049
TD Elongation (%)	351	358	357
MD Elmendorf Tear Strength (gm)	166	208	205

A linear regression analysis reveals that with the above fixed formulation, depth of activation water vapor transmission rate is predicted by the following equation:

$$\text{WVTR} = -329.73 + 31.216 * \text{Roller Temperature (°F)}$$

Changes and modifications in the specifically described embodiments can be carried out without departing from the scope of the invention which is intended to be limited only by the scope of the appended claims.

## CLAIMS

What we claim is:

1           1.     A process for imparting higher water vapor transmission rate (WVTR) to a filled  
2 polyolefin film comprising the steps of:  
3           extruding a polyolefin filler combination into a film; and  
4           passing said film through at least one pair of interdigitating grooved rollers wherein said  
5           rollers are heated to at least 80°F.

1           2.     The process as defined in Claim 1 wherein said interdigitating grooved rollers are  
2 positioned in a direction selected from the group including machine direction, transverse  
3 direction, and a combination thereof.

1           3.     The process as defined in Claim 2 wherein said polyolefin is selected from the  
2 group consisting of polypropylene, polyethylene, ethylene polar comonomer polymers,  $\alpha$ -olefin  
3 copolymers, and combinations thereof.

1           4.     The process as defined in Claims 1, 2, or 3 wherein said rollers are heated to at  
2 least 120 °F.

1           5.     The process as defined in Claims 1, 2, or 3 wherein said rollers are heated to at  
2 least 130 °F.

1           6.     The process as defined in Claims 1, 2, or 3 wherein said rollers are heated to at  
2 least 140 °F.

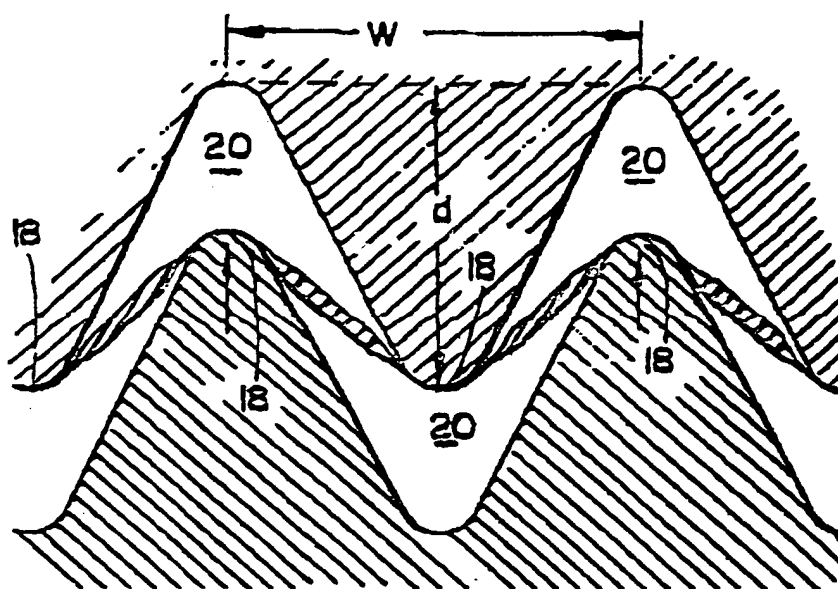
1           7.     The process as defined in Claims 1, 2, or 3 wherein said rollers are heated to at  
2 least 150 °F.

1           8       The process as defined in Claims 1, 2, or 3 wherein said rollers are heated to at  
2       least 160 °F.

1           9.       A process for imparting higher water vapor transmission rate (WVTR) in grams  
2       per square meter per day to a filled polyolefin film wherein the water vapor transmission rate is  
3       determined by the equation:

4                       
$$\text{WVTR} = -329.73 * 31.2162 (\text{Roller Temperature in } ^\circ\text{F})$$



**Figure 1.**

**Figure 2**

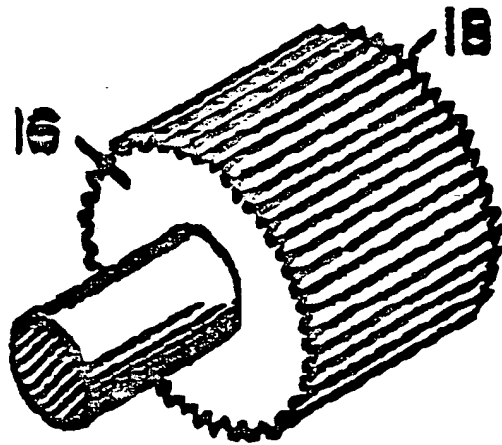
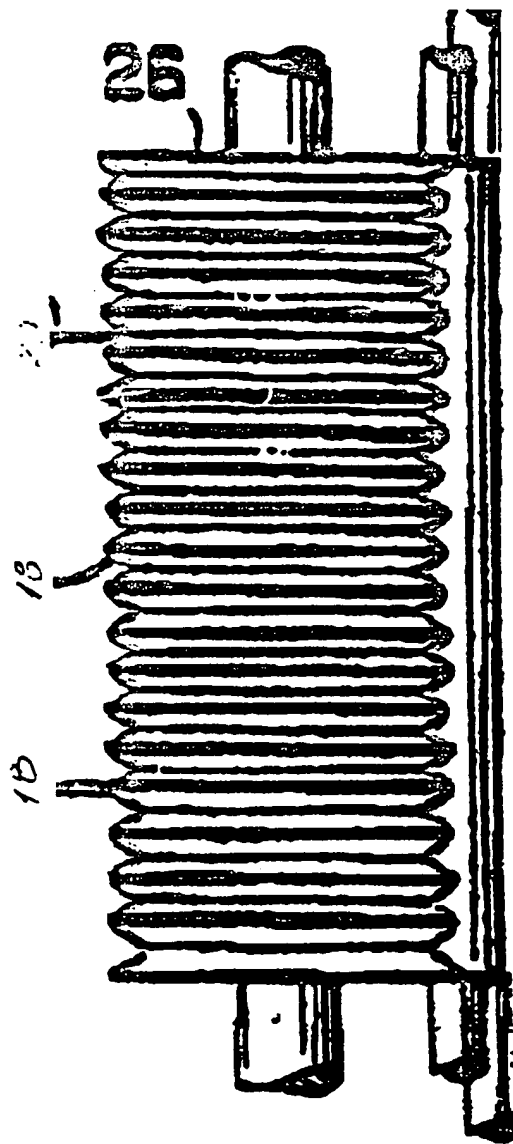


Figure 3



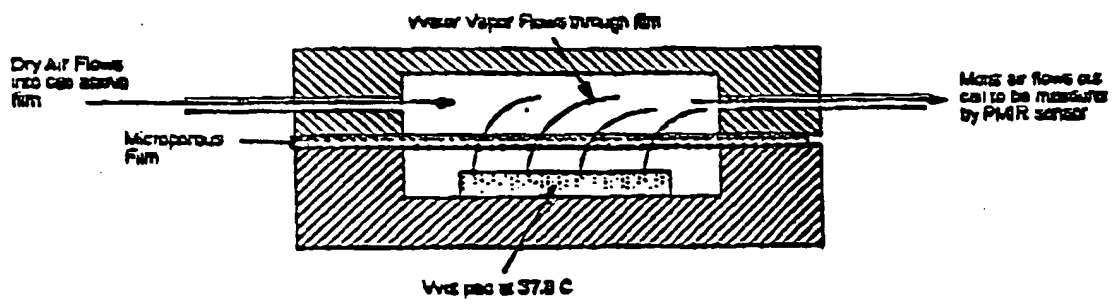


Figure 4

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/23879

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B29C55/18 //B29K23:00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 04397 A (EXXON CHEMICAL PATENTS INC) 5 February 1998 (1998-02-05) page 14, line 18 - line 21; claim 1	1-9
A	EP 0 550 115 A (DSM NV) 7 July 1993 (1993-07-07) page 3, line 31 - line 34; claim 10	1
A	EP 0 276 100 A (RASMUSSEN O B) 27 July 1988 (1988-07-27) page 6, line 64 -page 7, line 8 page 7, line 36 - line 39	1
A	US 4 806 300 A (WALTON RICHARD R ET AL) 21 February 1989 (1989-02-21) column 2, line 17 - line 36	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
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Attalla, G

# INTERNATIONAL SEARCH REPORT

Information on patent family members

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